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# Impact of internal crystalline boundaries on lattice thermal conductivity: Importance of boundary structure and spacing

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The low thermal conductivity of nano-crystalline materials is commonly explained via diffusive scattering of phonons by internal boundaries. In this study, we have quantitatively studied phonon-crystalline boundaries scattering and its effect on the overall lattice thermal conductivity of crystalline bodies. Various types of crystalline boundaries such as stacking faults, twins, and grain boundaries have been considered in FCC crystalline structures. Accordingly, the specularity coefficient has been determined for different boundaries as the probability of the specular scattering across boundaries. Our results show that in the presence of internal boundaries, the lattice thermal conductivity can be characterized by two parameters: (1) boundary spacing and (2) boundary excess free volume. We show that the inverse of the lattice thermal conductivity depends linearly on a non-dimensional quantity which is the ratio of boundary excess free volume over boundary spacing. This shows that phonon scattering across crystalline boundaries is mainly a geometrically favorable process rather than an energetic one. Using the kinetic theory of phonon transport, we present a simple analytical model which can be used to evaluate the lattice thermal conductivity of nano-crystalline materials where the ratio can be considered as an average density of excess free volume. While this study is focused on FCC crystalline materials, where inter-atomic potentials and corresponding defect structures have been well studied in the past, the results would be quantitatively applicable for semiconductors in which heat transport is mainly due to phonon transport. © *2014 AIP Publishing LLC*.
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Over the last decade, miniaturized and nano-structured crystalline systems have gained a lot of attention as potential candidates for thermoelectric applications because of their low thermal conductivities.[1–4] It has been shown that, with a relatively little change in electrical properties, the thermal conductivity of crystalline materials at small scales can be drastically reduced by the presence of free surfaces, internal defects, and boundaries where the system sizes or the constituent's micro-structural sizes are comparable to the phonon mean free path.[5–8] A fundamental challenge facing the applicable design of these miniaturized/nano-structured crystalline systems is a lack of a quantitative determination of phonon scattering at crystalline boundaries and free surfaces.

Several experimental and computational attempts have been carried out to study the lattice thermal conductivity of miniaturized crystalline systems with at least one dimension in the nanometer range, such as thin films, nano wires, and nano particles.[8–10] However, recently, it has been shown that internal defects may have a major contribution in the thermal conductivity reduction rather than free surfaces.[11–14] Therefore, beside confining the dimension of systems, introducing or removing of defects and boundaries can be considered as an alternative method to tailor the lattice thermal conductivity of crystalline materials.[12,15,16] Hence, it is crucial to explore and quantify the phonon scattering across crystalline boundaries. In the early 1950s, using dislocation theory and modeling the grain boundary as an array of dislocation, some analytical models for phonon scattering at low angle grain boundaries have been proposed.[17,18] According to them, phonon relaxation time has an inverse correlation with the square of grain boundary misfit angle. However, the linear dislocation theory and the dislocation picture of grain boundaries fail for high angle grain boundaries, where complex atomic structures are expected. In addition, it has been shown that there is no linear correlation between grain boundary energy and misfit angle,[19,20] and more ordered atomic structures may be obtained for grain boundaries with higher misfit angles. Hence, misfit angle may not be an accurate parameter to characterize phonon-boundary scattering. While distinguishing the electron and phonon contributions to the thermal conductivity of crystalline materials would be extremely difficult in experiments, atomistic simulations do not suffer this limitation. In this study, using systematic molecular dynamics (MD) simulations, we quantitatively explore the diffusive/specular phonon scattering through crystalline boundaries and its effect on the overall lattice thermal conductivity. Accordingly, the specularity coefficient will be determined for each boundary as the probability of phonon specular transmission at the boundaries. Finally, the relation of this parameter with boundary energy and excess free volume will be discussed and an analytic model will be proposed.

From a theoretical point of view and as a simple approximation, the lattice thermal conductivity $k$ can be calculated using well known kinetic theory[18,21] as

$$k = \frac{1}{3}\tau_{ph} C_V v_g^2, \tag{1}$$

where $C_V$ and $v_g$ are the specific heat capacity and phonon group velocity. $\tau_{ph}(x)$ is the phonon relaxation time which is

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calculated using the well known Matthiessen's rule[22] where all the phonon scattering mechanisms including phonon-surface scattering are taken into account[21]

$$\frac{1}{\tau_{ph}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{boundary}}. \quad (2)$$

In Eq. (2), $\tau_{ph}$ combines the phonon relaxation time of the bulk crystal $\tau_{bulk}$ with the one associated to the phonon-boundary scattering mechanism through $\tau_{boundary}$. Two scattering mechanisms are considered: (1) phonon-free surface and (2) phonon-internal boundaries scattering. This leads to the relation[21]

$$\frac{1}{\tau_{boundary}} = (1-h_f)\frac{2v_g}{D_f} + (1-h_b)\frac{2v_g}{D_b}, \quad (3)$$

where $D_f$ is the characteristic length of the structure (e.g., the distance between free surfaces) and $D_b$ is the microstructural length of the system (e.g., distance between internal boundaries). Note that the factor 2 in Eq. (3) appears because a phonon travels on average half the distance between boundaries before being scattered.[23,24] It has been shown that this would be a good approximation for the Debye model at temperatures higher than 80 K for polycrystalline silicon.[25] The empirical parameters $h_f$ and $h_b$ define the probability of specular scattering at free surfaces and internal boundaries, respectively.[21,26] A unity value for any of these parameters corresponds to the pure specular case, where boundary scattering does not contribute to the thermal conductivity, while a zero value corresponds to the pure diffusive scattering where Eq. (3) reduces to the well-known Casimir limit.[27] Recently, several expressions have been suggested for $h_f$ as a function of surface roughness.[11,28] For simplicity, we ignore the effect of free surface roughness and consider pure diffusive phonon scattering at the free surfaces, i.e., $h_f = 0$. However, diffusive versus specular nature of phonon scattering mechanisms across the internal boundary will be taken into account via the $h_b$ parameter. Since the phonon group velocity is weakly affected by system dimensions,[29] we consider that the phonon group velocity is independent of the domain size and rewrite Eq. (1) using Eqs. (2) and (3) as follows:

$$\frac{1}{k} = \frac{3}{v_g C_V}\left(\frac{1}{\lambda_\infty} + \frac{2}{D_f} + (1-h_b)\frac{2}{D_b}\right), \quad (4)$$

where $\lambda_\infty = \tau_{bulk} v_g$ is the bulk phonon mean free path.

In the context of molecular dynamics simulations, a recently developed approach[30] has been utilized to efficiently and accurately extract the overall lattice thermal conductivity of a nano-structure containing defects. To do so, we first minimized the system at temperature 100 K. Then, a heat impulse corresponding to temperature 150 K is imposed as a boundary condition on one side of the computational domain and the temperature evolution will be measured on the other side (see the inset of Figure 1). Comparing the temperature evolution with the analytic solution obtained from Fourier heat equation reveals the lattice thermal conductivity of the system.

In the first part of the study, we use Mishin Embedded Atom Method (EAM) potential[31] for crystalline Aluminum.

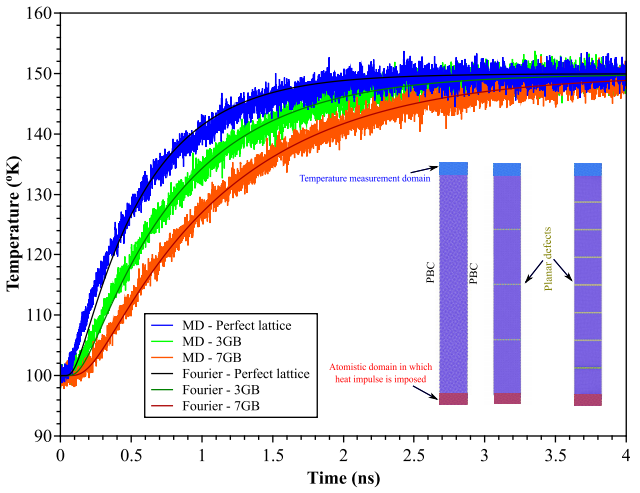


FIG. 1. Temperature evolution profile obtained from MD simulations and Fourier solutions for different inter-spacing between Σ13(510) grain boundaries in aluminum crystal for a constant system size (90 nm height and 15 nm cross section). Inset shows the schematic of the MD simulation.

Later, we examine other EAM potentials corresponding to copper[32] and gold[33] to extend the results. In all the simulations, we use periodic boundary conditions for lateral sides to suppress the free surfaces contribution to the lattice thermal conductivity. However, it has been shown that thermal conductivity is strongly size dependent in the direction of the heat flow, while the lateral free surface effect is negligible for large enough cross sections.[23,24,34] To characterize and validate the material properties required for the theoretical model (Eq. (4)), we first perform systematic simulations on defect-free crystals at different temperatures. Accordingly, to compromise between the predictive accuracy and the computational cost, we choose 15 nm cross section and 90 nm height samples for all the remaining simulations.[35]

Next, we introduce several boundaries into the system with specific inter-spacing corresponding to the desired boundary density. We focus our attention on symmetric planar defects such as the stacking fault, twin, and symmetric tilt grain boundaries to prevent the crystal anisotropy effect on the lattice thermal conductivity. The result in this study is mainly presented for FCC crystalline materials where interatomic potentials and corresponding defect structures are well studied in the past.

Figure 1 shows the temperature evolution profiles of crystal structures with different densities of a particular grain boundary Σ13(510). It can be seen that increasing the boundary density (i.e., decreasing boundary inter-spacing) delays temperature evolution. The obtained temperature evolution profiles are foreground with the Fourier predictions in Figure 1. Accordingly, the thermal diffusivity and corresponding lattice thermal conductivity for each crystalline system can be obtained. Similar results are also obtained for other types of crystalline boundaries.

Figure 2 summarizes the results of the MD simulations of the systems with various boundary structures and densities. The contribution of the free surfaces is a constant value since the system height, $D_b$, remains fix in all the simulations. Therefore, to focus our attention on the internal boundary effect, we rewrite Eq. (4) to distinguish the

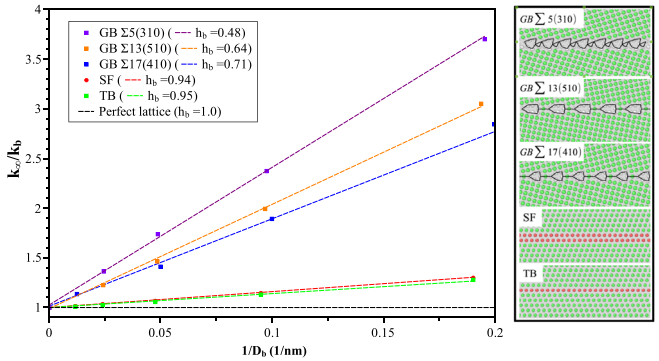


FIG. 2. Normalized inverse lattice thermal conductivity versus inverse boundary inter-spacing for different types of crystalline boundaries. Dashed lines are the analytical prediction using Eq. (5) for different values of $h_b$.

contribution of internal boundaries to the lattice thermal conductivity $k_b$ as follows:

$$\frac{1}{k_b} = \frac{1}{k} - \frac{3}{v_g C_V}\left(\frac{2}{D_f}\right) = \frac{3}{v_g C_V}\left(\frac{1}{\lambda_\infty} + (1-h_b)\frac{2}{D_b}\right). \quad (5)$$

For the sake of conciseness, in the remaining part of the paper, we will refer to $k_b$ as the lattice thermal conductivity. As shown in Figure 2, the inverse of the lattice thermal conductivity has a linear correlation with the inverse of the boundary spacing for all considered boundary structures. In other words, the lattice thermal conductivity reduces by increasing the boundary density. Similar observations have been recently reported for grain boundaries in 2D graphene sheet,[13] Si/Ge interface,[36] and nano-crystalline silicon.[25,37]

From Figure 2, it can be seen that for the boundaries whose atomic structures are very close to the perfect crystal (coherent boundaries such as twin boundary and stacking fault), there is only a negligible effect on the overall lattice thermal conductivity. This reveals that the phonon scattering is more specular for these coherent boundaries. This observation ensures that enhanced mechanical properties with a negligible loss of thermal conductivity can be obtained by introducing twin boundaries into crystalline systems.[7,38] Note that imperfections like dislocations and voids on twin boundaries and stacking faults may further reduce the lattice thermal conductivity. For crystalline boundaries with more complex atomic structures (non-coherent), such as grain boundaries, a significant effect on the overall lattice thermal conductivity is observed. For instance, as shown in Figure 2 the lattice thermal conductivity decreases by a factor larger than 2 for a crystal miniaturized with 10 nm spaced Σ5(310) grain boundaries. Therefore, phonon scattering across these non-coherent boundaries is expected to be more diffusive. A similar phenomenon has been experimentally observed where the electrical conductivity of a nano-twinned copper sample was very close to its bulk value, however, it was much lower for polycrystalline copper with nano-sized grains.[7]

To quantitatively characterize the phonon-boundary scattering and its effect on the overall lattice thermal conductivity, we compare Eq. (5) with the MD simulation results (dashed lines in Figure 2). Accordingly, the specularity coefficient $h_b$ for individual crystalline boundaries is obtained. Next, we examine two characteristic quantities associated with individual boundary structures: boundary energy and atomic excess free volume.[19,39–41] The boundary energy is defined as the excess free energy associated with the presence of a grain boundary, with the perfect lattice as the reference point in a unit area of the boundary.[19] The boundary excess free volume with a dimension of length has been considered as a measure of the local atomic disorder at boundaries.[20,39] Some recent efforts have been done to experimentally[42] and computationally[19,43] measure the excess free volume for various types of grain boundaries. From an atomistic point of view, the boundary excess free volume can be computed as a difference between the volume of a crystal with an internal boundary and a perfect one with the same number of atoms in a unit area of the grain boundary. Recent atomistic simulations of particular grain boundaries in silicon[44,45] show that a rather disordered, high-energy grain boundary has a significantly lower thermal conductivity than a more ordered, lower-energy one. However, a qualitative picture of this relation has not yet been explored. Similarly, the reduction of the electrical conductance in presence of imperfections/defects due to the scattering caused by the atomic disorder has been reported for gold.[16]

Figure 3 shows the variation of specularity coefficient as functions of the boundary energy and atomic excess free volume. Although a crystal boundary with higher energy causes a higher diffusive phonon scattering and consequently a larger reduction in the overall lattice thermal conductivity, no strong correlation is observed between the boundary energy and the corresponding specularity coefficient. In particular, the stacking fault energy is twice that of the twin boundary energy, although their specularity coefficients are very close to each other.

On the other hand, Figure 3 shows a strong correlation between the boundary specularity coefficient and the atomic boundary excess free volume. Careful analysis of the atomic structure for the stacking fault and the twin boundary reveals that the excess free volume for these coherent boundaries is very close to the perfect crystal. This can be understood by noting that in FCC crystalline metals, these faults are formed by displacing one or two (111) stacking planes parallel to the boundary plane. In this case, the atomic distance and

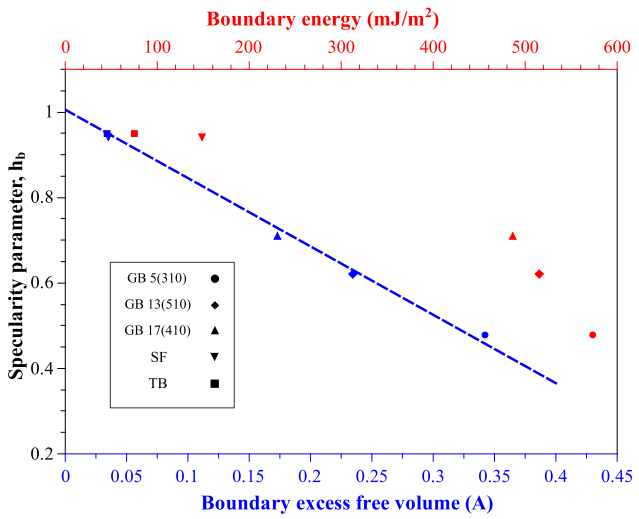


FIG. 3. Specular coefficient $h_b$ versus boundary excess free volume and boundary energy for different crystalline boundaries in aluminum.

consequently the excess free volume does not change considerably in the direction perpendicular to the boundary plane. Therefore, the specularity coefficient is close to 1 for these planar defects and the boundary-scattering effect on the lattice thermal conductivity is negligible. In contrast, a larger excess free volume is observed for non-coherent boundaries and consequently, a bigger specularity coefficient is also expected for them. For instance, the specularity coefficient for Σ5(310) grain boundary is smaller than 0.5, which reflects the diffusive nature of the phonon-scattering across it. Conclusively, it has been discovered that independently of the complex atomic structure of the boundary, its excess free volume dictates the phonon-boundary scattering in crystalline materials. This observation shows that phonon scattering across crystalline boundaries is mainly a geometrically favorable process rather than an energetical one. This is in agreement with a classical analytical model for low angle grain boundaries,[17] which showed that the phonon-boundary scattering correlates with the misfit angle of the boundary.

Next, we extend the obtained results to other crystalline metals. We perform a similar set of simulations for gold and copper.[35] To combine the results for different materials, we normalize Eq. (5) as

$$\frac{k_\infty}{k_b} = 1 + 2(1 - h_b)\frac{\lambda_\infty}{a}\frac{1}{n}, \tag{6}$$

where we rewrite the boundary spacing $D_b$ in terms of $n$ number of atomic layers of size $a$ (the lattice parameter which is material dependent). The non-dimensional parameter $(1 - h_b)\frac{\lambda_\infty}{a}$ is plotted versus the normalized boundary excess free volume for various crystalline boundaries in Figure 4. It can be seen that the specularity parameter for different crystalline boundaries and different materials can still be characterized via the excess free volumes. As seen in Fig. 4 and figured out previously,[46] the grain boundary excess free volume for copper is in general higher than the ones in gold and aluminum. Thus, a further reduction of the thermal conductivity due to the grain boundaries is expected for copper than for gold and aluminum.

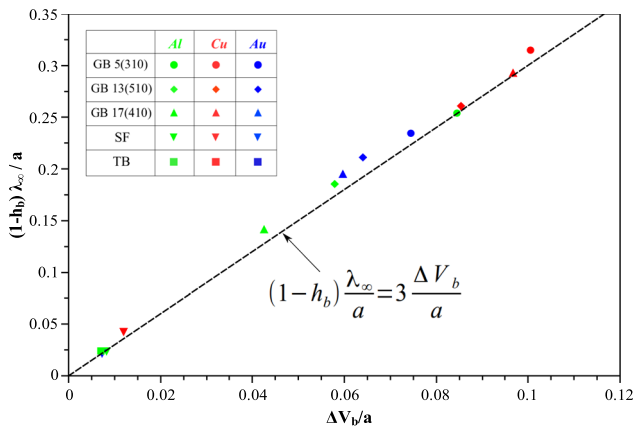


FIG. 4. Normalized boundary excess free volume versus normalized specular coefficient for different types of crystalline boundaries in various FCC metals.

Using Figure 4, Eq. (6) is rewritten for a general case as

$$\frac{k_\infty}{k_b} = 1 + 6\frac{\Delta V_b}{D_b}. \tag{7}$$

Remarkably, for the range of parameters studied herein, it can be seen that all data collapse on a single fit depicted by Eq. (7). It shows that the non-dimensional ratio of boundary excess free volume over boundary spacing directly correlates with the lattice thermal conductivity reduction in the presence of crystalline boundaries. In addition, as expected, similar results have been observed using a simple Lennard-Jones inter-atomic potential, which shows the generality of the model for metallic systems with different types of crystal lattice.

For nanostructured materials, the ratio of boundary excess free volume over boundary spacing can represent the average density of excess free volume which can be measured experimentally.[42] This result highlights the importance of introducing coherent boundaries such as twin in nanocrystalline materials to enhance the mechanical strength accompanying with a very negligible lattice thermal conductivity reduction.[7] In addition, this simple model can be used to approximately predict the lattice thermal conductivity of noncrystalline materials and optimally design miniaturized nano-structures for thermoelectric applications.[3,47] However, the electron contribution need be considered to fully characterize thermal conductivity of metallic systems. This study and the proposed model can be also useful for semiconductor materials where the phonon transport is known as the main mechanism for heat transfer.[48–50] Work on quantifying the proposed model for semiconductors is under way and initial results show similar trends for crystalline silicon.

Using atomistic simulations, we have quantitatively studied phonon-crystalline boundaries scattering and its effect on the overall lattice thermal conductivity of crystalline bodies. Considering various types of boundaries such as stacking faults, twins, and grain boundaries, we have shown that in the presence of internal boundaries, the lattice thermal conductivity can be characterized by the corresponding boundary spacing and boundary excess free volume. It has been shown that the lattice thermal conductivity of crystalline systems has an inverse linear relation with their internal boundary density. Additionally, we have demonstrated the direct correlation between the boundary specularity coefficient and its excess free volume. This observation confirms that the scattering nature of phonons across boundaries can be characterized by the local atomic spacing at the boundary. Conclusively, it has been shown that in the presence of internal boundaries, the non-dimensional ratio of boundary excess free volume over boundary spacing governs the lattice thermal conductivity of crystalline systems. Using the kinetic theory of phonon transport, we have presented a simple analytical model which can be used to evaluate the lattice thermal conductivity of nano-crystalline materials. Inversely, the excess free volume of a crystalline boundary can be measured via its thermal conductance.

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[1]D. Li, S. T. Huxtable, A. R. Abramson, and A. Majumdar, "Thermal transport in nanostructured solid-state cooling devices," J. Heat Transfer **127**, 108–114 (2005).
[2]G. J. Snyder and E. S. Toberer, "Complex thermoelectric materials," Nat. Mater. **7**, 105–114 (2008).
[3]L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, and M. G. Kanatzidis, "Ultralow thermal conductivity and high thermoelectric figure of merit in snse crystals," Nature **508**, 373–377 (2014).
[4]R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, "Thin film thermoelectric devices with high room-temperature figures of merit," Nature **413**, 597–602 (2001).
[5]M. Asheghi, Y. K. Leung, S. S. Wong, and K. E. Goodson, "Phonon-boundary scattering in thin silicon layers," Appl. Phys. Lett. **71**, 1798 (1997).
[6]W. Kim, S. L. Singer, A. Majumdar, J. M. O. Zide, D. Klenov, A. C. Gossard, and S. Stemmer, "Reducing thermal conductivity of crystalline solids at high temperature using embedded nanostructures," Nano Lett. **8**, 2097–2099 (2008).
[7]L. Lu, Y. Shen, X. Chen, L. Qian, and K. Lu, "Ultrahigh strength and high electrical conductivity in copper," Science **304**, 422–426 (2004).
[8]Y. K. Koh, "Heat transport by phonons in crystalline materials and nanostructures," Ph.D. dissertation (University of Illinois at Urbana-Champaign, 2010).
[9]D. Li, Y. Wu, P. Kim, L. Shi, P. Yang, and A. Majumdar, "Thermal conductivity of individual silicon nanowires," Appl. Phys. Lett. **83**, 2934–2936 (2003).
[10]J. Chen, G. Zhang, and B. Li, "Remarkable reduction of thermal conductivity in silicon nanotubes," Nano Lett. **10**, 3978–3983 (2010).
[11]Y. He and G. Galli, "Microscopic origin of the reduced thermal conductivity of silicon nanowires," Phys. Rev. Lett. **108**, 215901 (2012).
[12]K. F. Murphy, B. Piccione, M. B. Zanjani, J. R. Lukes, and D. S. Gianola, "Strain- and defect-mediated thermal conductivity in silicon nanowires," Nano Lett. **14**, 3785–3792 (2014).
[13]A. Bagri, S.-P. Kim, R. S. Ruoff, and V. B. Shenoy, "Thermal transport across twin grain boundaries in polycrystalline graphene from nonequilibrium molecular dynamics simulations," Nano Lett. **11**, 3917–3921 (2011).
[14]S. F. Karg, V. Troncale, U. Drechsler, P. Mensch, P. D. Kanungo, H. Schmid, V. Schmidt, L. Gignac, H. Riel, and B. Gotsmann, "Full thermoelectric characterization of inas nanowires using mems heater/sensors," Nanotechnology **25**, 305702 (2014).
[15]H. F. Zhan, Y. Y. Zhang, J. M. Bell, and Y. T. Gu, "Thermal conductivity of si nanowires with faulted stacking layers," J. Appl. Phys. **47**(1), 015303 (2014).
[16]D. J. Oliver, J. Maassen, M. E. Ouali, W. Paul, T. Hagedorn, Y. Miyahara, Y. Qi, H. Guo, and P. Grutter, "Conductivity of an atomically defined metallic interface," Proc. Natl. Acad. Sci. **109**, 19097–19102 (2012).
[17]P. G. Klemens, "The scattering of low-frequency lattice waves by static imperfections," Proc. Phys. Soc., London, Sect. A **68**, 1113 (1955).
[18]J. M. Ziman, "The general variational principle of transport theory," Can. J. Phys. **34**, 1256–1273 (1956).
[19]M. A. Tschopp and D. L. Mcdowell, "Asymmetric tilt grain boundary structure and energy in copper and aluminium," Philos. Mag. **87**, 3871–3892 (2007).
[20]D. Wolf, "Structure-energy correlation for grain boundaries in fcc metals-i: Boundaries on the (111) and (100) planes," Acta Metall. Mater. **37**, 1983–1993 (1989).
[21]"Introduction to nanoscale thermal conduction," in *Heat Transfer - Mathematical Modelling, Numerical Methods and Information Technology*, edited by A. Belmiloudi (InTech, 2011).
[22]A. Matthiessen and C. Vogt, "On the influence of temperature on the electric conducting-power of alloy," Philos. Trans. R. Soc. **154**, 167–200 (1864).
[23]Y. Zhou, B. Anglin, and A. Strachan, "Phonon thermal conductivity in nanolaminated composite metals via molecular dynamics," J. Chem. Phys. **127**, 184702 (2007).
[24]S. Wang, X. G. Liang, X. Xu, and T. Ohara, "Thermal conductivity of silicon nanowire by nonequilibrium molecular dynamics simulations," J. Appl. Phys. **105**, 014316 (2009).
[25]Z. Wang, J. E. Alaniz, W. Jang, J. E. Garay, and C. Dames, "Thermal conductivity of nanocrystalline silicon: Importance of grain size and frequency-dependent mean free paths," Nano Lett. **11**, 2206–2213 (2011).
[26]R. Chen, A. I. Hochbaum, P. Murphy, J. Moore, P. Yang, and A. Majumdar, "Thermal conductance of thin silicon nanowires," Phys. Rev. Lett. **101**, 105501 (2008).
[27]H. Casimir, "Note on the conduction of heat in crystals," Physica **5**, 495–500 (1938).
[28]G. Xie, Y. Guo, B. Li, L. Yang, K. Zhang, M. Tang, and G. Zhang, "Phonon surface scattering controlled length dependence of thermal conductivity of silicon nanowires," Phys. Chem. Chem. Phys. **15**, 14647–14652 (2013).
[29]K. Imamura, Y. Tanaka, and S. Tamura, "Group velocities of phonons in superlattices," Phys. Rev. B **65**, 174301 (2002).
[30]G. Anciaux and J. Molinari, "A molecular dynamics and finite elements study of nanoscale thermal contact conductance," Int. J. Heat Mass Transfer **59**, 384–392 (2013).
[31]Y. Mishin, D. Farkas, M. Mehl, and D. Papaconstantopoulos, "Interatomic potentials for monoatomic metals from experimental data and *ab initio* calculations," Phys. Rev. B **59**, 3393 (1999).
[32]Y. Mishin, M. J. Mehl, D. A. Papaconstantopoulos, A. F. Voter, and J. D. Kress, "Structural stability and lattice defects in copper: *Ab initio*, tight-binding, and embedded-atom calculations," Phys. Rev. B **63**, 224106 (2001).
[33]G. Grochola, S. P. Russo, and I. K. Snook, "On fitting a gold embedded atom method potential using the force matching method," J. Chem. Phys. **123**, 204719 (2005).
[34]P. Heino and E. Ristolainen, "Thermal conduction at the nanoscale in some metals by md," Microelectron. J. **34**, 773–777 (2003).
[35]See supplementary material at http://dx.doi.org/10.1063/1.4901887 for more information on material parameters and molecular dynamic simulations.
[36]M. Hu and D. Poulikakos, "Si/ge superlattice nanowires with ultralow thermal conductivity," Nano Lett. **12**, 5487–5494 (2012).
[37]T. S. English, J. L. Smoyer, J. C. Duda, P. M. Norris, T. E. Beecham, and P. E. Hopkins, "Modeling grain boundary scattering and thermal conductivity of polysilicon using an effective medium approach," in ASME/JSME 2011 8th Thermal Engineering Joint Conference (2011).
[38]J. Wang, F. Sansoz, J. Huang, Y. Liu, S. Sun, Z. Zhang, and S. X. Mao, "Near-ideal theoretical strength in gold nanowires containing angstrom scale twins," Nat. Commun. **4**, 1742 (2013).
[39]H. Aaron and G. Bolling, "Free volume as a criterion for grain boundary models," Surf. Sci. **31**, 27–49 (1972).
[40]"Correlation between the structure and energy of grain boundaries in metals," in *Materials Interfaces: Atomic-Level Structure and Properties*, edited by D. Wolf (Springer, 1992).
[41]Y. Kuru, M. Wohlschlogel, U. Welzel, and E. J. Mittemeijer, "Large excess volume in grain boundaries of stressed, nanocrystalline metallic thin films: Its effect on grain-growth kinetics," Appl. Phys. Lett. **95**, 163112 (2009).
[42]E.-M. Steyskal, B. Oberdorfer, W. Sprengel, M. Zehetbauer, R. Pippan, and R. Wurschum, "Direct experimental determination of grain boundary excess volume in metals," Phys. Rev. Lett. **108**, 055504 (2012).
[43]T. Uesugi and K. Higashi, "First-principles calculation of grain boundary energy and grain boundary excess free volume in aluminum: Role of grain boundary elastic energy," J. Mater. Sci. **46**, 4199–4205 (2011).
[44]C. Kimmer, S. Aubry, A. Skye, and P. K. Schelling, "Scattering of phonons from a high-energy grain boundary in silicon: Dependence on angle of incidence," Phys. Rev. B **75**, 144105 (2007).
[45]P. K. Schelling, S. R. Phillpot, and P. Keblinski, "Kapitza conductance and phonon scattering at grain boundaries by simulation," J. Appl. Phys. **95**, 6082 (2004).
[46]D. Wolf, "Structure-energy correlation for grain boundaries in fcc metals-iii: Symmetrical tilt boundaries," Acta Metall. Mater. **38**, 781–790 (1990).
[47]Y. Zhang, E. Skoug, J. Cain, V. Ozolin, D. Morelli, and C. Wolverton, "First-principles description of anomalously low lattice thermal conductivity in thermoelectric cu-sb-se ternary semiconductors," Phys. Rev. B **85**, 054306 (2012).
[48]P. Caroff, K. A. Dick, J. Johansson, M. E. Messing, K. Deppert, and L. Samuelson, "Controlled polytypic and twin-plane superlattices in iii v nanowires," Nat. Nanotechnol. **4**, 50–55 (2009).
[49]K. A. Dick, C. Thelander, L. Samuelson, and P. Caroff, "Crystal phase engineering in single inas nanowires," Nat. Nanotechnol. **10**(9), 3494–3499 (2010).
[50]S. Dhara, H. S. Solanki, R. A. Pawan, V. Singh, S. Sengupta, B. A. Chalke, A. Dhar, M. Gokhale, A. Bhattacharya, and M. M. Deshmukh, "Tunable thermal conductivity in defect engineered nanowires at low temperatures," Phys. Rev. B **84**, 121307 (2011).